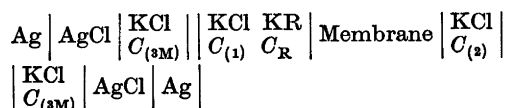


The Donnan Potential. I

TORMOD FØRLAND^a and TERJE ØSTVOLD^b

^aThe University of Trondheim, Norwegian Institute of Technology, Division of Physical Chemistry, Trondheim, Norway and ^bThe University of Trondheim, College of Arts and Science, Chemistry Department, Trondheim, Norway

The Donnan potential is calculated on the basis of classical irreversible thermodynamics for the following galvanic cell:

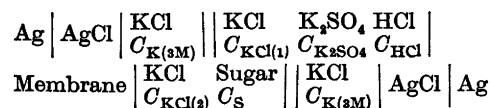


The membrane is permeable to water, K^+ and Cl^- ions, but impermeable to R^- ions. When chemical equilibrium has been established across the membrane for KCl and H_2O , the emf calculated for the present cell may be approximated by the equation:

$$E = \frac{RT}{F} \left\{ \ln \frac{C_{(\text{K}_1)}}{C_{(\text{K}_2)}} + \ln \left(1 + \frac{(u_{\text{R}} - u_{\text{Cl}}) C_{\text{R}}}{(u_{\text{K}} + u_{\text{Cl}}) C_{\text{K}(sM)}} \right) \right\}$$

where the subscripted C 's and u 's denote, respectively, the concentrations and mobilities of the different ions in the solution. It is important to note that the potential given by this equation, according to the formalism applied in the present paper, is created in the two KCl salt bridges and not as usually stated in the area of the membrane.

The Donnan potential is a concept very commonly used in biophysics, and it is frequently used in calculations on transport processes across biological membranes. It is defined as the electric potential difference between membrane and solution at the membrane-solution interface. In a recent paper Førland and Østvold (1973)¹ calculated the total potential for the cell



Acta Chem. Scand. A 28 (1974) No. 6

The membrane was considered permeable to water and K^+ and Cl^- ions. Chemical equilibrium was assumed established for KCl and H_2O across the membrane.

Since it is generally assumed that the liquid junctions at the two salt bridges do not create any emf, it is supposed that the emf is created across the membrane. Since there is a concentration gradient of K^+ (and Cl^-) ions over the membrane, it has, of course, been tempting to apply the Nernst equation to this concentration gradient and calculate the corresponding potential difference, which immediately leads to the equation

$$E = \frac{RT}{F} \ln \frac{C_{\text{K}(1)}}{C_{\text{K}(2)}} \quad (1)$$

This equation was derived by Donnan and by Guggenheim (1932)² and is in agreement with the results obtained for the above mentioned cell by the present authors.¹ The extensive agreement between theory and experiment has made this emf calculation widely accepted. However, since it inherently contains some not well defined quantities, a critical analysis of the above method of calculation ought to be made.

The only measurable potential difference is the total emf of the cell, but in the above treatment this has been split up into two liquid junctions and one membrane potential (in addition to the potentials of the two identical electrodes), which are not measurable quantities. Furthermore, the ratio $C_{\text{K}(1)}/C_{\text{K}(2)}$ is an approximation for the activity ratio of potassium ions, and activities of ions are also immeasurable.

The fundamental equation for calculating the emf of a reversible galvanic cell is:

$$\Delta G + FE = 0 \quad (2)$$

where ΔG is the total change in Gibbs energy in the cell per Faraday transferred. Eqn. (2) is based on the first and second law of thermodynamics.

If, in addition to the process connected to the charge transfer, an irreversible diffusion process takes place in the cell, the problem can be dealt with within the framework of irreversible thermodynamics.

Due to the irreversible diffusion that takes place and due to the charge transfer itself, the Gibbs energy of the cell will change during charge transfer. It may be shown from the postulated of irreversible thermodynamics [Førlund (1960)³ and Førlund, Thulin and Østvold (1971)⁴] that the Gibbs energy change can be separated into two parts, one time dependent, $\Delta G_{(t)}$, and one dependent on the electric charge transferred, $\Delta G_{(Q)}$, and that only the last one is connected to the external emf, E :

$$\Delta G_{(Q)} + FE = 0 \quad (3)$$

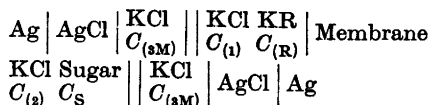
This equation is the same as eqn. (2) for a cell with reversible reactions only.

The main difference between the method of emf calculation expressed by eqn. (3) and that expressed by an equation like eqn. (1), is that in the former no attempt is made to calculate any quantity that cannot be measured, whereas in the latter operations concerning immeasurable quantities are introduced. In most cases these immeasurable quantities will be combined in the final result yielding a measurable quantity, the calculated emf of the cell, so that the two approaches give the same final answer. However, problems may arise in applications of the latter method whenever it is desirable to include physical interpretations in the course of the calculations, e.g. in connection with the introduction of approximations.

Equations like eqn. (1) give detailed information on the sources of the electric potential difference. In the case of the present cell, this is across the membrane, even though it cannot be verified by measurements. Eqn. (3), on the other hand, can tell us in an exact way the situation in cell where the cause of the measured emf is to be found, since contributions to $\Delta G_{(Q)}$ are well defined measurable quantities in any section of the cell.

The statement that the electrical potential difference over the cell according to eqn. (1) is created over the membrane, is in contradiction with the results obtained using the more fundamental eqns. (2) or (3).

Let us in the following discussion try to resolve this contradiction and let us use the following galvanic cell to demonstrate our ideas:



The membrane is permeable to water and K^+ and Cl^- ions but impermeable to the larger anion R^- . Chemical equilibrium is assumed established for KCl and H_2O across the membrane. This cell is also shown schematically in Fig. 1.

Since the membrane is permeable to K^+ and Cl^- only (the transport of water may be disregarded at the moment), charge transfer across the membrane will be connected with a change in the content of KCl in the electrolyte on the two sides of the membrane. The extent of the change in KCl content on each side is dependent on the transport numbers in the

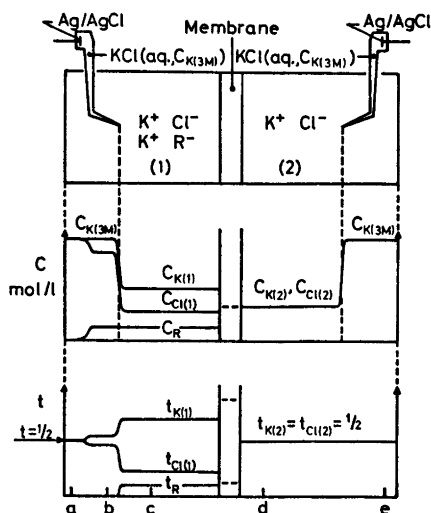


Fig. 1. A schematic diagram of a special galvanic cell constructed to study the Donnan potential together with diagrams of the variations of the concentration of the K^+ , Cl^- , and R^- ions and the transport numbers of the K^+ , Cl^- , and R^- ions throughout the cell.

membrane. However, these transport numbers are of no interest in the emf calculation, since transport of KCl in this region occurs over ranges with constant chemical potential ($\mu_{\text{KCl}(1)} = \mu_{\text{KCl}(2)}$). Thus, the contribution to $\Delta G_{(Q)}$, and therefore also to the emf, by charge transfer is zero in the electrolyte close to the membrane and in the membrane.

This has been a problem to several scientists working in the field of membrane potentials [see Babcock and Overstreet (1953)⁵ and Bull (1971)⁶]. When there is no contribution to $\Delta G_{(Q)}$ in the region of the membrane, the next question arise; Where is the measured electric work generated? The only source left is the liquid junction to the KCl bridge, even though such contacts are generally believed not to contribute to an emf.

We will consider the transport of components from the left hand side of the cell. The mobilities of K^+ and Cl^- ions are approximately equal. The ratio $C_{\text{K}}/C_{\text{Cl}}$ is unity in the 3 M solution, but it is greater than unity in the KCl-KR mixture. Therefore the transport number of K^+ ions is increasing from left to right in the liquid junction (water is chosen as frame of reference). Consequently KCl must be transported from a high to a low concentration region when a positive charge is passed from left to right in the cell. This must be the main contribution to $\Delta G_{(Q)}$ and thus to the observed emf.

The following derivation is carried out for the sake of the scientist interested in the alternative approach to emf calculations making use of well defined measurable quantities only.

The cell considered is the one shown in Fig. 1. In the following calculation the assumption of ideal solution and constant ionic mobilities will be introduced. However, the method of calculation possesses the same rigidity as the laws of thermodynamics themselves. Since only measurable quantities are dealt with, it is always possible to check the approximations introduced in the calculation by measurements.

The change in Gibbs energy due to charge transfer and the emf are connected by eqn. (3). Calculation of $\Delta G_{(Q)}$ requires knowledge of the transport numbers and chemical potential of the components along the whole length of the cell [see, e.g., Førland, Thulin and Østvold (1971)⁴].

$$\Delta G_{(Q)} = \Delta G_{\text{el}} - \int_{\text{over cell}} \sum_i \mu_i dt_i \quad (4)$$

where ΔG_{el} is the change in Gibbs energy in the vicinity of the electrodes. In the present cell the two electrodes and their surroundings are identical, so $\Delta G_{\text{el}} = 0$. The integral $-\int \sum_i \mu_i dt_i$ is the change in Gibbs energy due to change in composition by the charge transfer in the different sections of the cell. In any region where all transport numbers t_i are constant, the change in Gibbs energy is zero.

If we are to strictly restrain ourselves to measured quantities in our derivation of the emf, and not introduce and unnecessary assumptions about the ionic species present in our system, both μ_i and t_i should refer to neutral components. The transport coefficient, t_i , simply expresses the result of an Hittorf transport experiment, where it is found by chemical analysis that a quantity t_i of component i has moved from left to right in a Hittorf cell, when 1 Faraday is passed through the cell. Such a transport coefficient for a neutral component will depend on the kind of electrodes used.

In a transport experiment it is necessary to define a frame of reference relative to which the movements of the components are expressed. The most commonly used reference frame in experiments on aqueous solutions is the water itself. For systems with a membrane it may sometimes be more practical to use the membrane as a frame of reference. The correlation between the two kinds of corresponding transport coefficients is of course given by the transport of water through the membrane during charge transfer.

For the present cell, where the Gibbs energy change during charge transfer is zero in the region of the membrane, it is most practical to use the water as frame of reference.

From eqn. (4) we have:

$$\Delta G_{(Q)} = - \int (\mu_{\text{KCl}} dt_{\text{KCl}} + \mu_{\text{KR}} dt_{\text{KR}}) \quad (5)$$

Here t_{KCl} and t_{KR} are, respectively, the number of moles of KCl and KR transported from left to right per Faraday transferred in a Hittorf cell with electrodes reversible to the Cl^- ion as shown in Fig. 2.

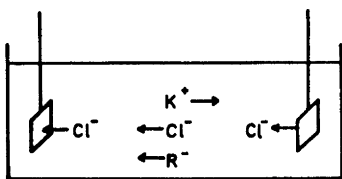


Fig. 2. The Hittorf experiment with electrodes reversible to the Cl^- ion.

Wanting to express the result of the Hittorf experiment in terms of the ionic transport numbers, it may easily be seen that:

$$t_{\text{KCl}} = t_{\text{K}} + t_{\text{R}} = 1 - t_{\text{Cl}}$$

and

$$t_{\text{KR}} = -t_{\text{R}}$$

thus

$$dt_{\text{KCl}} = -dt_{\text{Cl}} \text{ and } dt_{\text{KR}} = -dt_{\text{R}} \quad (6)$$

Introducing eqn. (6) into eqn. (5) we obtain

$$\Delta G_{(Q)} = \int_{a \rightarrow e} \mu_{\text{KCl}} dt_{\text{Cl}} + \int_{a \rightarrow e} \mu_{\text{KR}} dt_{\text{R}} \quad (7)$$

Fig. 1 shows how the concentration changes along the length of the cell. It should be noticed that the liquid junction for the KCl bridge on the left hand side is made in a special way. Some KR is dissolved into the 3 M KCl solution. Thus, in this liquid junction the content of one component (with respect to the water content) remains approximately constant while the other one is changing. This makes it possible to calculate the contribution to $\Delta G_{(Q)}$ in the liquid junction without introducing the Henderson (1907, 1908)⁷ or Planck (1890)⁸ approximations. In a recent paper experimental and calculated potentials for concentration cells containing the above mentioned type of gradients were compared.*

Calculation of $\Delta G_{(Q)}$ in eqn. (7) may be simplified by the use of partial integration:

$$\Delta G_{(Q)} = \left| t_{\text{Cl}} \mu_{\text{KCl}} - \int_{a \rightarrow e} t_{\text{Cl}} d\mu_{\text{KCl}} \right| + \left| t_{\text{R}} \mu_{\text{KR}} - \int_{a \rightarrow e} t_{\text{R}} d\mu_{\text{KR}} \right| \quad (8)$$

Since the two electrodes are identical the terms $\left| t_{\text{Cl}} \mu_{\text{KCl}} \right|_{a \rightarrow e} = 0$.

Since $\lim_{x \rightarrow 0} x \ln x = 0$ the term $\left| t_{\text{R}} \mu_{\text{KR}} \right|_{a \rightarrow e} = 0$

*To be published.

Furthermore, the integral over the range $c \rightarrow d$

$$\int_{c \rightarrow d} t_{\text{Cl}} d\mu_{\text{KCl}} = 0 \text{ because } d\mu_{\text{KCl}} = 0 \text{ in this range}$$

and

$$\int_{c \rightarrow d} t_{\text{R}} d\mu_{\text{KR}} = 0 \text{ because } d\mu_{\text{KR}} = 0 \text{ in the range}$$

where $t_{\text{R}} \neq 0$

The terms left in eqn. (8) are:

$$\Delta G_{(Q)} = - \int_{a \rightarrow c} t_{\text{Cl}} d\mu_{\text{KCl}} - \int_{d \rightarrow e} t_{\text{Cl}} d\mu_{\text{KCl}} - \int_{a \rightarrow c} t_{\text{R}} d\mu_{\text{KR}} \quad (9)$$

Using the present formalism it is evident that no contribution to $\Delta G_{(Q)}$ is created in the area of the membrane and therefore no emf can be produced in this section of the cell.

From eqn. (9) an exact calculation of $\Delta G_{(Q)}$, and thus of the emf, may be carried out when the chemical potential and transport numbers are known as functions of composition.

When such data are not at hand, an approximate calculation may be carried out by assuming ideal solutions and constant ionic mobilities. Since the mobilities of K^+ and Cl^- are approximately equal, $t_{\text{Cl}} \approx \frac{1}{2}$ in the range $d \rightarrow e$. The transport numbers of Cl^- and R^- may be expressed as:

$$t_{\text{Cl}} = \frac{u_{\text{Cl}} C_{\text{Cl}}}{\sum_i u_i C_i} \text{ and } t_{\text{R}} = \frac{u_{\text{R}} C_{\text{R}}}{\sum_i u_i C_i}$$

where

$$\sum_i u_i C_i = u_{\text{K}} C_{\text{K}} + u_{\text{Cl}} C_{\text{Cl}} + u_{\text{R}} C_{\text{R}} = (u_{\text{K}} + u_{\text{Cl}}) C_{\text{K}} + (u_{\text{R}} - u_{\text{Cl}}) C_{\text{R}}$$

The assumption of ideal solution gives:

$$d\mu_{\text{KCl}} = RT d \ln C_{\text{K}} C_{\text{Cl}} \text{ and } d\mu_{\text{KR}} = RT d \ln C_{\text{K}} C_{\text{R}}$$

In the following integration this approximation is applied over a very large concentration range. However, the major contribution to the integrals will lie in the range of low concentrations. (This may also be observed from the final result of this calculation.)

In the range $a \rightarrow b$ C_{R} and C_{Cl} vary, and $dC_{\text{R}} = -dC_{\text{Cl}}$

In the range $b \rightarrow c$ C_{K} and C_{Cl} vary, and $dC_{\text{K}} = dC_{\text{Cl}}$

Introducing the above approximations into eqn. (9) we obtain

$$\frac{\Delta G_{(Q)}}{RT} = - \int_a^b t_{Cl} \frac{dC_{Cl}}{C_{Cl}} - \int_a^b t_R \frac{dC_R}{C_R} - \int_b^c t_{Cl} \times \left(\frac{dC_K}{C_K} + \frac{dC_{Cl}}{C_{Cl}} \right) - \int_a^b t_R \frac{dC_K}{C_K} - \frac{1}{2} \ln C_{K(sM)}^2 + \frac{1}{2} \ln C_{K(s)}^2$$

and

$$\frac{\Delta G_{(Q)}}{RT} = - \int_a^b \frac{(u_R - u_{Cl})dC_R}{(u_K + u_{Cl})C_{K(sM)} + (u_R - u_{Cl})C_R} - \int_a^b \frac{u_{Cl} - u_K}{\sum u_i C_i} dC_K - \int_a^b \frac{dC_K}{C_K} - \ln C_{K(sM)} + \ln C_{K(s)}$$

Since $u_{Cl} = u_K$, we obtain

$$\frac{\Delta G_{(Q)}}{RT} = - \frac{C_R = C_R}{C_R = 0} \ln \{ (u_K + u_{Cl})C_{K(sM)} + (u_R - u_{Cl})C_R \}$$

$$- \frac{C_{K(1)}}{C_{K(sM)}} \ln C_K - \ln C_{K(sM)} + \ln C_{K(s)}$$

and

$$\frac{\Delta G_{(Q)}}{RT} = - \ln \left\{ 1 + \frac{(u_R - u_{Cl})C_R}{(u_K + u_{Cl})C_{K(sM)}} \right\} + \ln \frac{C_{K(s)}}{C_{K(1)}} \quad (10)$$

The emf of the Donnan cell will therefore be equal to

$$E = \frac{RT}{F} \left[\ln \frac{C_{K(1)}}{C_{K(s)}} + \ln \left\{ 1 + \frac{(u_R - u_{Cl})C_R}{(u_K + u_{Cl})C_{K(sM)}} \right\} \right] \quad (11)$$

The last term will generally be very small since $C_{K(sM)} \gg C_R$, and the expression for the emf will be the same as eqn. (1). It is, however, important to note that the potential given by eqn. (11), according to the present formalism, is created in the two KCl salt bridges and not in the area of the membrane.

This surprising result, namely that the potential created across the membrane is zero, is a consequence of the alternative way proposed for splitting the total cell potential in electrode and junction contribution which now are expressed by measurable and thermodynamically well defined quantities.

The advantage of the above derivation of eqn. (11) lies in the fact that only quantities which are well defined by measurements are used, that each operation in the derivation is easily visualized physically, that the approximations introduced may be judged experimentally, and that one can see how the calculation can be carried out more accurately when better data are available.

REFERENCES

1. Førland, T. and Østvold, T. *Acta Chem. Scand.* 27 (1973) 2199.
2. Donnan, F. G. and Guggenheim, E. A. *Z. Phys. Chem. (Leipzig)* 162 (1932) 346.
3. Førland, T. *Acta Chem. Scand.* 14 (1960) 1381.
4. Førland, T., Thulin, L. U. and Østvold, T. *J. Chem. Educ.* 48 (1971) 741.
5. Babcock, K. L. and Overstreet, R. *Science* 117 (1953) 686.
6. Bull, H. B. *An Introduction to Physical Biochemistry*, F. H. Davis Company, Philadelphia, 1971, p. 178.
7. Henderson, P. Z. *Phys. Chem. (Leipzig)* 59 (1907) 118; 63 (1908) 325.
8. Planck, M. *Ann. Phys. (Leipzig)* 39 (1890) 161; 40 (1890) 561.

Received January 21, 1974.